R & D NOTES

Band-Aging Catalyst Deactivation: Analytical Solutions

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In the operation of adiabatic fixed-bed reactors subject to a substantially exothermic reaction, it is widely recognized that the reaction rate accelerates rapidly as the temperature increases through the catalyst bed. When catalyst deactivation simultaneously occurs, the bed length is increased to permit continued commercial operation while a portion of the bed has deactivated. For this exothermic case, the temperature rises rapidly at the bed inlet, and deactivation occurs mainly at this inlet zone. With increasing time on stream, the effect of deactivation is to move the zone of rapid temperature increase further down the bed. This progressive movement of the temperature profile through a deactivating fixed bed of catalyst, in a band of high temperature, has been termed a band-aging catalyst deactivation problem (Penick et al. 1983).

This problem has been of historical importance in slowly deactivating systems, such as water-gas shift reactors and methanation reactors. It has also become of recent importance in the Mobil M-gasoline process using ZSM-5 catalyst, wherein the band-aging problem occurs over a cycle time of about a week, after which catalyst regeneration is required. Clearly, it would be very desirable to provide analytical solutions to the complex equations describing such systems, for such solutions would facilitate data interpretation, reactor design, and cycle time optimization.

In the simulation of an adiabatic reactor, at least two coupled nonlinear differential equations must be solved, for the relevant mass and energy balances. With simultaneous catalyst deactivation, the catalyst activity is further dependent upon time, temperature, and distance through the bed. In general, this simulation problem can be addressed only by numerical solution procedures. In the present communication, a band-aging deactivation problem is solved analytically by exponential integral techniques (Douglas and Eagleton, 1962). This problem consists of slow deactivation (pseudosteady state) of a plug-flow reactor by feed poisons with low sensitivity to temperature due to the complete adsorption of the poison by the solid catalyst.

Theoretical Development

Consider a first-order reaction with associated deactivation, as may have applicability to a methanation reactor (Willey and Kittrell, 1984). The reaction rate, at a catalyst activity of a, is expressed as:

$$r = ka\,(C_A)_f(1 - x) \tag{1}$$

For a plug-flow reactor in which the time of deactivation is long compared to the reactor response time, a pseudosteady state mass balance becomes:

$$\frac{Q_f}{S}\frac{dx}{dz} = ka\,(1 - x) \tag{2}$$

The energy balance for such an adiabatic reactor is:

$$\frac{1}{S}\frac{dT}{dz} = \frac{(-\Delta H)\,r}{Q\rho C_p} \tag{3}$$

If the volumetric flow rate through the reactor is essentially constant, then $Q = Q_f$, and Eqs. 2 and 3 are combined to provide:

$$\frac{dt}{dz} = \frac{(-\Delta H)(C_A)_f}{\rho C_p}\frac{dx}{dz} \tag{4}$$

If $\Delta H/\rho C_p$ can also be taken as constant throughout the bed, then this equation may be integrated directly to yield:

$$T = T_o + \frac{(-\Delta H)\,(C_A)_f\,x}{\rho C_p} \tag{5}$$

where T_o is the temperature at $x = 0$. The reactor conversion

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profile then requires a solution of Eq. 2 through the relationship of the rate constant to temperature:

$$k = A \exp(-E/RT) \tag{6}$$

For the deactivating catalyst, the activity term in Eq. 2 must also be considered. Wheeler and Robell (1969) have solved the plug-flow reactor problem for deactivation by a feed poison, to yield:

$$a = \frac{\exp(\beta_1 z)}{\exp(\beta_1 z) + \exp(\beta_2 \tau) - 1} \tag{7}$$

Furthermore, for many cases including essentially complete poison adsorption, β_1 and β_2 are not strongly temperature-dependent. Hence, Eq. 2 becomes, upon substitution,

$$\frac{Q_f}{S}\frac{dx}{dz} = A \exp\left(\frac{-E}{RT}\right) \frac{\exp(\beta_1 z)}{\exp(\beta_1 z) + \exp(\beta_2 \tau) - 1}(1 - x) \tag{8}$$

where T is given by Eq. 5. Let us define the additional parameters:

$$\alpha_1 = \frac{E}{R}$$

$$\alpha_2 = \frac{-\Delta H\,(C_A)_f}{\rho C_p}$$

$$\alpha_3 = \frac{SA}{Q}$$

$$\alpha_4 = \beta_1$$

$$\alpha_5 = \exp(\beta_2 \tau) - 1$$

Then, Eq. 8 becomes:

$$\int_0^x \exp\left(\frac{\alpha_1}{T_o + \alpha_2 x}\right)\frac{dx}{(1 - x)} = \int_0^z \alpha_3 \frac{\exp(\alpha_4 z)}{\exp(\alpha_4 z) + \alpha_5}\,dz \tag{9}$$

Applying the method of partial fractions, the lefthand side of Eq. 9 may be written in terms of exponential integrals:

$$-\int_{\alpha_1/T_o}^{y} \frac{\alpha_2 + T_o}{(\alpha_2 + T_o)\,y - \alpha_1} e^y\,dy + \int_{\alpha_1/T_o}^{y} \frac{e^y}{y}\,dy$$

$$= -\exp\left(\frac{\alpha_1}{T_o + \alpha_2}\right)\int_{w_o}^{w} \frac{e^w\,dw}{w} + \int_{y_o}^{y} \frac{e^y}{y}\,dy \tag{10}$$

where

$$y = \frac{\alpha_1}{T_o + \alpha_2 x} \tag{11a}$$

$$w = y - \frac{\alpha_1}{\alpha_2 + T_o} \tag{11b}$$

$$y_o = \alpha_1/T_o \tag{11c}$$

$$w_o = y_o - \frac{\alpha_1}{\alpha_2 + T_o} \tag{11d}$$

Upon integration of the righthand side of Eq. 9 and the substitution of Eq. 10:

$$-\exp\left(\frac{\alpha_1}{\alpha_2 + T_o}\right)[Ei(w) - Ei(w_o)] + Ei(y) - Ei(y_o)$$

$$= \alpha_3\left\{z - \frac{1}{\alpha_4}\ln\left[\frac{1 + \alpha_5 \exp(-\alpha_4 z)}{1 + \alpha_5}\right]\right\} \tag{12}$$

where the exponential integral is

$$Ei(y) = \int_{-\infty}^{y} \frac{\exp(s)}{s}\,ds \tag{13}$$

Equation 12 may be used to determine the conversion as a function of time and position in the catalyst bed. Activity profiles are obtained from Eq. 7 and temperature profiles from Eq. 5. Obviously, other forms of deactivation expressions can be used as long as an analytical solution can be found for the righthand side of Eq. 9.

Example

Carbon monoxide is removed from a hydrogen stream by methanation in a tubular reactor 1.8 m in dia. and 5.3 m long. The following reaction is applicable: $CO + 3H_2 \rightarrow CH_4 + H_2O$.

The feed contains 2 mol % CO and enters at 288°C at a rate of 22.9 m^3/s. The operating pressure is 10 atm. The reactor is adiabatic, packed with a nickel catalyst, which deactivates due to a sulfur contaminant in the feed. The CO reaction is pseudofirst-order, due to the large excess of hydrogen.

The mass balance for this reaction is given by Eq. 2, with a rate constant of

$$k = 6.07 \times 10^{12} \exp\left(\frac{-30{,}000}{1.987\,T}\right) \tag{14}$$

Taking $\Delta H = -50{,}000$ cal/mol, $(C_A)_f = 4.3$ mol/m^3, $\rho = 187.5$ mol/m^3, and $C_p = 7.7$ cal/mol · K:

$$\frac{(-\Delta H)\,(C_A)_f}{\rho C_p} = 149\text{ K} \tag{15}$$

reducing the energy balance to:

$$dT = 149\,dx \tag{16}$$

The constants for the activity expression of Eq. 7 are:

$$\beta_1 = 1.932\text{ m}^{-1}$$

$$\beta_2 = 0.00075\text{ h}^{-1}$$

$$\alpha_1 = 15{,}100\text{ K}$$

$$\alpha_2 = 149\text{ K}$$

$$\alpha_3 = 6.75 \times 10^{11}\text{ m}^{-1}$$

$$\alpha_4 = 1.932\text{ m}^{-1}$$

$$\alpha_5 = \exp(0.00075\,\tau) - 1$$

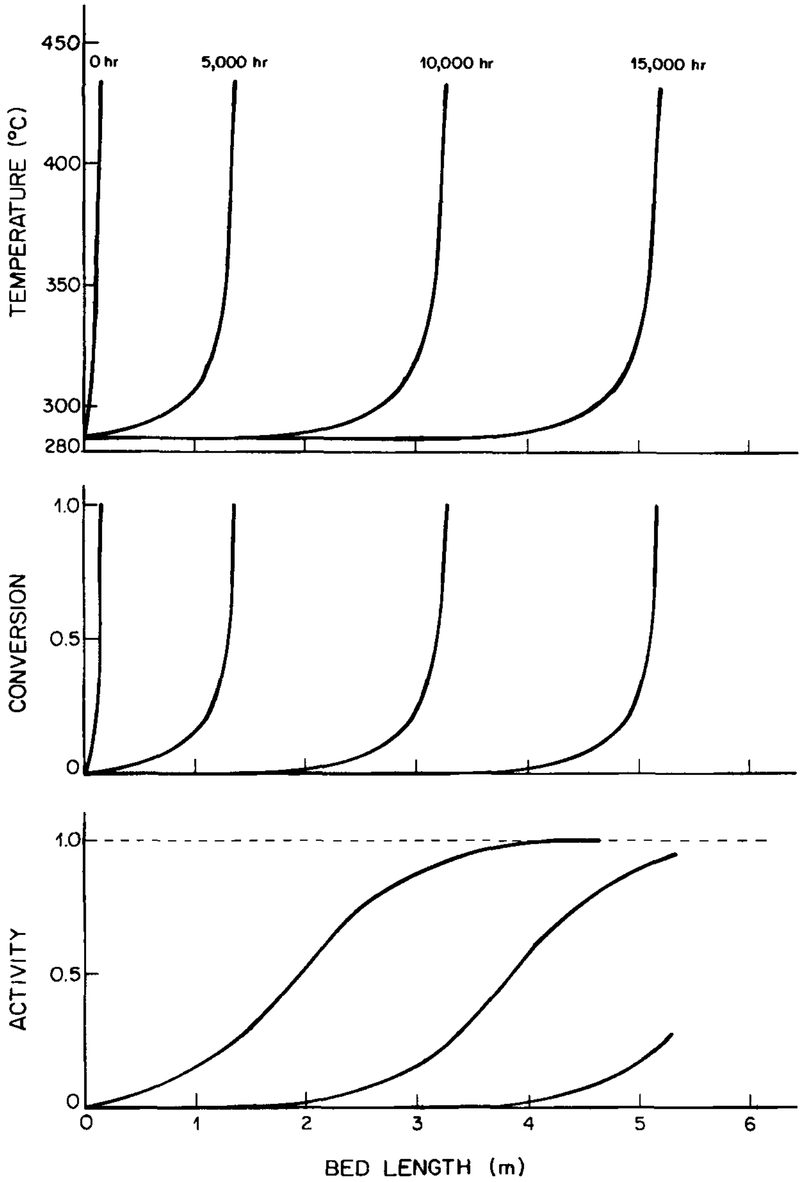

Figure 1. Profiles of temperature, conversion, and activity in adiabatic methanation reactor with catalyst deactivation.

This set of nonlinear, coupled differential equations was solved analytically by the method derived above. The plots of temperature, conversion, and activity in the catalyst bed at 0, 5,000, 10,000, and 15,000 h vs. position are shown in Figure 1.

Notation

A = frequency factor in Arrhenius equation, s^{-1}
a = catalyst activity, dimensionless
$(C_A)_f$ = reactant concentration in feed, mol/m^3
C_p = heat capacity, cal/mol · K
E = activation energy, cal/mol
E_i = exponential integral
k = first order reaction rate constant, s^{-1}
Q = volumetric flow rate in reactor, m^3/s
Q_f = volumetric feed rate, m^3/s
R = gas constant, 1.987 cal/mol · K
r = rate of reaction, mol/m^3 · s
s = dummy variable in exponential integral
T = temperature, K
S = cross-sectional area of reactor, m^2
x = conversion, dimensionless
z = distance through the bed, m
β's = constant coefficients of the activity equation, β_1 in m^{-1}, β_2 in h^{-1}
ΔH = heat of reaction, cal/mol
τ = time on stream, h
ρ = density, mol/m^3

Literature cited

Douglas, J. M., and L. C. Eagleton, *I&EC Fundamentals*, **1**(2), 116 (1962).

Penick, J. E., W. Lee, and J. Maziuk, *Am. Chem. Soc. Symp. Ser.*, **226**, 19 (1983).

Wheeler, A., and A. J. Robell, *J. Catalysis*, **13**, 299 (1969).

Willey, R. J., and J. R. Kittrell, *I&EC Prod. Res. & Dev.*, **23**, 206 (1984).

Manuscript received Apr. 3, 1985, and revision received Oct. 14, 1985.